Preparation of Dense $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ Ceramic by Controlling the Defect Structure

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欠陥制御による高密度 $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ 焼結体の作製

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The improvement of the sintering properties of a superconducting $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic by the introduction of point defects was examined. In order to introduce Ba vacancies into the structure, a mixture of BaCO_3 , Pb_3O_4 and Bi_2O_3 , with Ba-deficient nominal composition, was used as a starting material. The density of the specimen increased by using this nominally Ba-deficient mixture. However, it was revealed that the grain size in the sintered material was not affected by the amount of the nominal Ba deficiency and that a second phase, composed mainly of Bi and oxygen, was generated at grain boundaries. It was concluded that Ba vacancies could not be formed in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ lattice and that the apparent high density and electrical resistivity, which was as high as $10^{-1} \Omega \cdot \text{cm}$ at room temperature, is attributed to the second phase formation at grain boundaries. When sintering under low oxygen partial pressure, the density of the superconducting $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic also increased. However, it was observed that the grain size of the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic increased without the generation of a second phase at grain boundaries while sintering under reducing atmosphere. The dependence of the grain size on the oxygen partial pressure led to the suggestion that enhanced grain growth is governed by the increase of volume diffusion due to the introduction of oxygen vacancies. After annealing under oxygen to remove oxide ion vacancies, the specimen showed an electrical resistivity at room temperature as low as $10^{-3} \Omega \cdot \text{cm}$ and a sharp superconducting transition at 11.5 K.

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1. Introduction

$\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ is a superconducting oxide with a transition temperature of $\sim 11 \text{ K}$.¹⁾ Despite the low transition temperature compared to the so-called high- T_c superconducting cuprates, we regard the analysis of the conduction mechanism of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ highly significant since $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ can be seen as a prototype of high- T_c cuprates, because its crystal structure is a simple distorted-perovskite structure.²⁾ So far, various methods such as electrical conductivity measurement,³⁾ Hall measurement,^{3),4)} Seebeck measurement^{5),6)} have been applied to analyze the conduction mechanism of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$. One of the problems, however, which must be overcome in order to analyze its conduction property, is the difficulty to prepare sintered bodies with high density.

Thanh et al. reported that sintering under mechanical pressure, so-called hot-pressing, was effective for the preparation of dense specimens.³⁾ However, it would be difficult to prepare specimens large enough for the characterization of conduction properties with their method. In order to improve the sintering characteristics, an enhanced element diffusion is required. One of the methods, which can be regarded as effective to enhance element diffusion, is simply the increase of sintering temperature. However, the composition of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ would vary during sintering above 900°C since Pb and Bi are volatile at such a high temperature.

The other probable method to enhance diffusion is the introduction of point defects into the specimen. For example,

the introduction of interstitial Zn ions was reported to be effective for the sintering of ZnO .^{7),8)} In the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ structure, a cubic closed packing of Ba and oxide ions is considered. Therefore, we assumed that an enhanced diffusion of Ba and/or oxide ions would be effective by improve the sintering properties of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$. In this study, the improvement of the sintering behavior of a $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic due to the introduction of Ba ions or oxide ion vacancies was examined.

2. Experimental

2.1 Preparation of the specimen with nominal Ba deficiency

To examine whether Ba vacancies could be introduced or not, the specimens with a nominal composition of $\text{Ba}_{1-x}\text{Pb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ($x=0.0-0.1$) were prepared from a mixture of BaCO_3 (99.9%), Pb_3O_4 (99.9%) and Bi_2O_3 (99.9%). They were mixed in ethanol and dried at 50°C for 24h, followed by calcination at 720°C for 12h in air. After pressed into pellet at a pressure of 300 kg/cm^2 , they were subjected to sintering at 800°C for 12h in air.

2.2 Preparation of sintered $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ under low oxygen partial pressure

The oxygen specimens with nominal composition of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ were also prepared from a mixture of BaCO_3 (99.9%), Pb_3O_4 (99.9%) and Bi_2O_3 (99.9%). They were mixed in ethanol and calcined at 720°C for 12h in air. After pressed into pellets, they were sintered at 840°C for 16h under various oxygen partial pressures, P_{O_2} , between

$1.01 \times 10^5 - 6.37$ Pa, in order to examine whether the sintering properties could be improved by the introduction of oxygen vacancies or not. P_{O_2} was monitored by a zirconia oxygen sensor (Toray LC750), equipped within the downstream of the furnace. Thermogravimetric measurements confirmed that oxygen vacancies are generated in $BaPb_{0.75}Bi_{0.25}O_3$ at 840°C under the above-mentioned P_{O_2} .⁹⁾ Heat treatment of the sintered pellets under 1.01×10^5 Pa of oxygen at 800°C for 16h and successively at 600°C for 24h was carried out in order to remove the oxygen vacancies again. The oxygen content of the specimen after annealing was confirmed to be 3.00 by thermogravimetry and iodometry.¹⁰⁾

2.3 Characterization

The apparent density was calculated from weight and volume of the specimens. To distinguish whether the specimens were composed of a single phase or not, X-ray diffraction patterns were recorded using a Rigaku RINT2400 instrument ($\text{Cu K}\alpha$, 40 kV, 200 mA). The electrical resistivity of the specimens was measured as a function of temperature by the standard four-probe method.¹⁰⁾ Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out to estimate grain size and compositional distribution of the specimens using a JSM-5200 (JEOL Co., Ltd.) and a JXA-8900 (JEOL Co., Ltd.) instrument, respectively.

3. Results and discussion

3.1 Sintering properties of the material with a nominal composition of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$

Figure 1 shows the dependence of the apparent density of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$ on the nominal Ba composition. The apparent density increased with the decrease of the nominal Ba content, showing that the sintering properties increased successfully with Ba deficiency. However, the electrical resistivity was also influenced by the Ba deficiency. Figure 2 shows the temperature dependence of the electrical resistivity for the specimens with $x=0.00$ (a), $x=0.05$ (b) and $x=0.10$ (c). A sharp superconducting transition was observed for every specimen at 11.5 K, however, the resistivity at normal state increased by more than one order of magnitude with the increase of x .

To clarify the reason for the increase of the electrical resistivity with x , X-ray diffraction and SEM-EPMA measurements were carried out. Figure 3 shows the X-ray diffraction patterns of the specimens with $x=0.00$ and $x=0.10$. All of the peaks can be indexed assuming an or-

thorhombic symmetry,⁹⁾ however, one additional weak peak was observed around $2\theta=28.25^\circ$, i.e., lattice spacing of 0.3157 nm, in the X-ray diffraction pattern of $x=0.10$. The X-ray diffraction peak at $2\theta=28.25^\circ$ of every specimen is shown in Fig. 4. The intensity of this peak increased with increasing x . Figure 5 shows the lattice constants of every specimen calculated from the respective X-ray diffraction patterns. The applied calculation method was described in a preceding paper.¹¹⁾ No variation of lattice constants was observed with increasing x . Thus, it was concluded that the

Fig. 4. X-ray diffraction peak around $2\theta=28.25^\circ$ for the specimens with a nominal composition of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$.

Fig. 5. Dependence of lattice constants of the specimens with a nominal composition of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$ on the nominal Ba content. No lattice constant variation on Ba content was observed.

Fig. 1

Fig. 2

Fig. 3

Fig. 1. Dependence of the apparent densities of the specimens with a nominal composition of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$ on the nominal Ba content.

Fig. 2. Dependence of the electrical resistivities of the specimens with a nominal composition of $Ba_{1-x}Pb_{0.75}Bi_{0.25}O_3$ on temperature. (a) $x=0.00$, (b) $x=0.05$ and (c) $x=0.10$.

Fig. 3. X-ray diffraction patterns of the specimens with a nominal composition of (a) $BaPb_{0.75}Bi_{0.25}O_3$ and (b) $Ba_{0.9}Pb_{0.75}Bi_{0.25}O_3$. All of the peaks can be indexed as orthorhombic symmetry except for the peak at $2\theta=28.25^\circ$ in (b). (compare Fig. 4)

formation of Ba vacancies did not generate in the BaPb_{0.75}Bi_{0.25}O₃ lattice, instead, an impurity phase was formed when a nominally Ba deficient mixture was used for synthesis.

Figure 6 shows SEM backscattering images of the polished surface of the specimen with (a) $x=0.00$ and (b) $x=0.10$. There was no significant difference between the size of the BaPb_{0.75}Bi_{0.25}O₃ grains of the specimens shown in Fig. 6(a) and Fig. 6(b). Besides the BaPb_{0.75}Bi_{0.25}O₃ grains, a second phase was observed at grain boundaries in the specimen depicted in Fig. 6(b). Bi, a little amount of Pb and oxygen, however, no Ba were detected in the secondary grain-boundary phase using EPMA. It can be concluded that the increase of the apparent density and the electrical resistivity with increasing Ba deficiency is not attributed to Ba vacancies in the lattice but to the generation of this second phase at the grain boundaries, composed mainly of excess Bi and oxygen.

3.2 Sintering properties of BaPb_{0.75}Bi_{0.25}O₃ heat-treated under low oxygen partial pressure

Figure 7 shows the dependence of the apparent density of BaPb_{0.75}Bi_{0.25}O₃ on the $\log P_{O_2}$ during sintering at 840°C. The apparent density increased with a decrease of $\log P_{O_2}$. Electrical resistivities of the specimens sintered under (a) 1.01×10^5 Pa of oxygen and (b) 6.37 Pa of oxygen, follow-

Fig. 6. Scanning backscattered electron images of the polished specimens with a nominal composition of (a) BaPb_{0.75}Bi_{0.25}O₃ and (b) Ba_{0.9}Pb_{0.75}Bi_{0.25}O₃.

Fig. 7

Fig. 8

Fig. 9

Fig. 7. Dependence of the apparent density of BaPb_{0.75}Bi_{0.25}O₃ on $\log P_{O_2}$ during sintering. Every specimen was subsequently annealed under 1.01×10^5 Pa of oxygen to remove oxygen vacancies after sintering.

Fig. 8. Dependence of the electrical resistivity of BaPb_{0.75}Bi_{0.25}O₃ sintered under an oxygen partial pressure of (a) 1.01×10^5 Pa and (b) 6.37 Pa. Both specimens were post-annealed under 1.01×10^5 Pa of oxygen to remove oxygen vacancies after sintering.

Fig. 9. Dependence of the lattice constants of BaPb_{0.75}Bi_{0.25}O₃ on $\log P_{O_2}$ during sintering. Every specimen was annealed under 1.01×10^5 Pa of oxygen to remove the oxygen vacancies after sintering. No variation of lattice constants was observed.

ed by annealing at 800°C and successively at 600°C in O₂ flow are shown in Fig. 8. Sharp superconducting transitions were observed at 11.5 K for both specimens. The lower electrical resistivity at normal state of the specimen in Fig. 8(b) as compared to (a) is considered to be due to the higher density of the specimen given in (b).

After annealing under 1.01×10^5 Pa of oxygen, all X-ray diffraction patterns of BaPb_{0.75}Bi_{0.25}O₃ could be indexed as orthorhombic symmetry and no X-ray diffraction peak assigned to an impurity phase was observed regardless of the oxygen partial pressure. Figure 9 shows the dependence of the lattice constants of BaPb_{0.75}Bi_{0.25}O₃, posterior to annealing under oxygen, on the $\log P_{O_2}$ during sintering. No variation of lattice constants with varying $\log P_{O_2}$ was observed, suggesting that the chemical composition and structure of the BaPb_{0.75}Bi_{0.25}O₃ phase did not vary with P_{O_2} during sintering and upon subsequent annealing under oxygen.

Figure 10 shows SEM images of fractured BaPb_{0.75}Bi_{0.25}O₃ sintered at 840°C under (a) 1.01×10^5 Pa, (b) 1.01×10^3 Pa and (c) 6.37 Pa of oxygen. After sintering, all of the specimens were annealed under 1.01×10^5 Pa of oxygen. No second phase was observed at the grain boundaries in any of the specimen, which is in agreement with the X-ray diffraction measurements. On the other hand, the grain size increased with decreasing P_{O_2} . Figure 11 shows the variation of grain size of BaPb_{0.75}Bi_{0.25}O₃ with $\log P_{O_2}$, measured from the SEM images depicted in Fig. 10. Almost all of the grains of BaPb_{0.75}Bi_{0.25}O₃, sintered under 1.01×10^5 Pa oxygen, were less than 6 μm in size. Decreasing the oxygen partial pressure during sintering to 1.01×10^3 Pa, increased the grain size up to $\sim 10 \mu\text{m}$. A grain size as large as $\sim 30 \mu\text{m}$ was observed in the specimen sintered under an oxygen partial pressure of 6.37 Pa.

The increase in grain size showed qualitative correspondence with the increase of apparent density with decreasing P_{O_2} , as depicted in Fig. 7. Figure 12 shows the dependence of the equilibrium oxygen nonstoichiometry, δ , of BaPb_{0.75}Bi_{0.25}O_{3- δ} on $\log P_{O_2}$ at 840°C.⁹⁾ The amount of oxygen vacancies, δ , increased with decreasing $\log P_{O_2}$, showing a qualitative agreement with the variation of grain size and apparent density with $\log P_{O_2}$. Therefore, it is assumed that oxygen vacancies, introduced during sintering under low P_{O_2} , enhanced the diffusion of oxygen vacancies and that grain growth was also enhanced by the increase of the oxygen vacancy diffusion coefficient, D_v . So far, the dependence of D_v on δ of BaPb_{0.75}Bi_{0.25}O_{3- δ} has not

Fig. 10. Scanning electron micrographs of fractured $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ sintered at 840°C under (a) 1.01×10^5 Pa, (b) 1.01×10^3 Pa and (c) 6.37 Pa of oxygen. Every specimen was post-annealed under 1.01×10^5 Pa of oxygen to remove the oxygen vacancies after sintering.

Fig. 11. Variation of grain size of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ on $\log P_{\text{O}_2}$ at sintering.

Fig. 12. Dependence of the equilibrium oxygen nonstoichiometry, δ , of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$ on $\log P_{\text{O}_2}$ at 840°C .⁹⁾

yet been reported. However, Mizusaki reported that D_v of BaBiO_3 was $\sim 10^{-5} \text{ cm}^2/\text{s}$ at 850°C , which is relatively high compared to those of other conducting oxides.¹²⁾ Since the crystal structure and chemical composition of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ are similar to those of BaBiO_3 , the authors expect a high D_v for $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$. The measurement of D_v of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$ is now in progress.

In this study, oxide ion vacancies were easily introduced in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$, while Ba vacancies were not. The authors suppose that for charge balance Pb and/or Bi must take a valence higher than $4+$ in order to incorporate Ba vacancy in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$, which should be very difficult. However, Pb and/or Bi must take a valence lower than $4+$, which is possible, for the introduction of oxide ion vacancies.

4. Conclusion

$\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic with high density could be prepared through solid state reaction of a nominally Ba deficient mixture. The high density of the nominally Ba deficient specimen was due to the generation of a second phase at the grain boundaries, composed mainly of Bi and oxygen. The density of the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ceramic could also be increased by sintering under low oxygen partial pressure. It was observed that the grain size increased with decreasing oxygen partial pressure. It was suggested that oxygen vacancies, generated during sintering under low oxygen partial pressure, enhanced the oxide ion vacancy diffusion.

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